Automobile adsorption air-conditioning system using oil palm biomass-based activated carbon: A review

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ABSTRACT

Refrigeration and air-conditioning technology are required to evolve in accordance to Montreal Protocol adopted in 1987 and Kyoto Protocol in 1997. This regulation concerns about the climate change in an attempt to phase-out chlorofluorocarbons (CFCs), followed by hydro-chlorofluorocarbons (HCFCs) and then moving to 1,1,1,2-tetrafluoroethane (HFC-134a) starting 2011. This trend leads to a strong demand of new systems for air-conditioning, especially in automobile. Adsorption cooling system, among other proposed cooling technologies, has a very good potential for automobile applications. Hence, there exists a need for a creative design and innovation to allow adsorption technology to be practical for air-conditioning in automobile in a near future. Oil palm shell-based activated carbon has been widely applied in various environmental pollution control technologies, mainly due to its high adsorption performance yet low cost. However, limited studies have been carried out on the characteristics and application of oil palm shell-based activated carbon in adsorption air-conditioning system. This paper is to present a comprehensive review on the past efforts in the field of adsorption air-conditioning systems for automobile. This work also aims to investigate the physicochemical properties of oil palm shell-based activated carbon and its feasibility for application in adsorption air-conditioning system. Some of the limitations are outlined and suggestions for future improvements are pointed out.

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1. Introduction

In general, automobile air-conditioning systems are designed to provide comfort for the driver and the passengers during a journey. The conventional electrical-driven compression systems are widely used in almost all of the automobiles today. However, air-conditioning technology is required to evolve due to the new environmental regulations, notably Montreal Protocol in 1987, Kyoto Protocol in 1997 and European Commission Regulation 2037/2000. These regulations are concerning about the depletion of the ozone layer and also global warming, which decided to phase-out CFCs and followed by HCFCs and HFC-134a. As a result, this trend has led to a strong demand for a new air-conditioning technology. Among the existing air-cooling technologies, adsorption air-cooling system has good energy-saving potential. The advantages of this system are: it can be powered by using waste heat or solar, long lasting, low maintenance cost, used non-polluting refrigerants and friendly to environment [1]. Unfortunately, no working prototype has been practically run in present automobiles due to various restrictions, due to sizing and cooling capacity limitations. Adsorption refrigeration cycle powered by solar energy or waste heat exhausted from engines has been successfully used for ice making and cold production. For example, carbon–ammonia solar refrigerator for vaccine cooling [2], solar adsorption ice maker [3], silica gel–water adsorption refrigeration cycle driven by waste heat of near-ambient temperature [4], zeolite–water solar cold storage system [5] and a combined solar thermoelectric-adsorption cooling system using activated carbon–methanol working pair [6]. Based on the cited literatures, extensive research has been performed on adsorption refrigeration, but research on the possibility of applying this technology for automobile air-conditioning purposes is still rare. Therefore this review paper focuses on the adsorption system for automobile air-conditioning purpose.

Activated carbons have been tested with various adsorbates as the working pair in adsorption cooling system [7–10], however, most of the activated carbons studied were commercially available activated carbons which were synthesized from expensive and non-renewable materials. Activated carbon derived from oil palm shell has been widely used in various applications especially in environmental control technologies such as for the adsorption of methane [11], hexavalent chromium [12], copper ions [13], 4-chloroguaiacol [14], phenol [15] and treatment of landfill leachate [16]. Oil palm shell-based activated carbon has been proved to give high adsorption performance, however limited studies have been carried out on the application of this activated carbon in adsorption air-conditioning systems.

Besides, not many studies have been carried out on the physicochemical properties of activated carbon which are the most significant parameters affecting the adsorption performance and the cooling efficiency of an adsorption cooling system. Adsorption characteristics of activated carbon can be determined by the adsorption isotherms, kinetics and mechanism. It is of importance to precisely analyze the performance of an adsorption cooling system, based on an accurate determination of the adsorbent–adsorbate behaviour and on an exact understanding of the influence of operating conditions and the working pair characteristics on the performance, including the evaluation of the adsorption capacity and rate of adsorption of the activated carbon on the adsorbate [7].

2. Activated carbon

Activated carbon encompasses a broad range of amorphous carbon-based materials having high degrees of porosity and extensive surface areas. The properties of each finished activated carbon are influenced by the starting materials used and by the conditions of activation. The result is a myriad of activated carbons, each having a specific utility. The method most frequently used for preparation of activated carbon involves carbonization of the precursors at high temperature in an inert atmosphere followed by activation. There are mainly two different methods for activation, namely physical and chemical. Physical activation process comprises treatment of the char obtained from carbonization with some oxidizing gases, generally steam or carbon dioxide at high temperature. The porous structure is created due to the elimination of volatile matter during pyrolysis and the carbon on the char is removed during activation. The main function of gasification is to widen the pores, creating large mesoporosity. In chemical activation, a chemical agent is impregnated to the precursors prior to heat treatment in an inert atmosphere. The pores are developed by dehydration and oxidation reactions of the chemicals.

Activated carbons find wide applications as adsorbents, catalyst or catalyst supports. Activated carbon is one of the most important adsorbents from an industrial point of view. The main application of this adsorbent is for separation and purification of gaseous and liquid phase mixtures. In general, activated carbons can be divided into gas-adsorbing and liquid-phase carbons. The main distinction between gas-adsorbing and liquid-phase carbons lies in the pore size distribution. Basically, the structure of activated carbons containing pores are classified according to the International Union of Pure and Applied Chemistry [17] classification into three groups, micropores (pore size < 2 nm), mesopores (pore size 2–50 nm) and macropores (pore size > 50 nm). Gas-adsorbing carbons usually have the most pore volume in the micropore and macropore ranges, whereas liquid-phase carbons have significant pore volume in the mesopore or transitional pore range, permitting ready access of liquids to the micropore structure which results in rapid attainment of adsorption equilibrium for smaller adsorbates.

Activated carbons concern many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, nuclear and automobile, because of their adsorptive properties due to high available surface area which is presented in their extensive internal pore structure. The high porosity of activated carbons is a function of both the precursor as well as the scheme of activation. Activated carbons are now frequently used in environmental processes for removing toxic gases and in wastewater as well as potable water treatments.

2.1. Properties and structures of activated carbon

Activated carbon has specific properties depending on the material source and the mode of activation. In both physical and chemical activation processes, knowledge of different variables is very important in developing the porosity of the activated carbon. The adsorption capacity of an activated carbon is related to its properties such as surface area, pore volume, pore size distribution and pore structure. The development of micropores and mesopores is important as it allows the activated carbon to adsorb large amounts and various types of adsorbates either from gas or liquid streams [18].

Activated carbons are materials having complex porous structures with associated energetic as well chemical inhomogeneities. Their structural heterogeneity is a result of existence of micropores, mesopores and macropores of different sizes and shapes [19]. The structure of an activated carbon is comprised of carbon atoms that are ordered in parallel stacks of hexagonal layers, extensively cross-linked and tetrahedrally bonded. Several heteroatoms including oxygen, hydrogen, nitrogen and others can be found in the carbon matrix in the form of single atoms and/or functional groups [20]. The large surface area of an activated carbon is associated with near-molecular size pores and capillaries formed within the carbon granules by selective burning and oxidation of raw material during activation. Commercial activated carbons typically have total surface area in the range from 450 to 1500 m^2/g as measured by the nitrogen adsorption method. The pore volumes of commercial activated carbons normally range from 0.5 to 1.5 cm^3/g [21].

2.2. Types of activated carbon

A challenge in activated carbon production is to produce very specific carbons with particular characteristics. The forms and characteristics of the activated carbons prepared are highly dependent on the precursors and the activation methods used. Different physical forms of activated carbons are produced depending on their applications [22]. The most common forms by which activated carbons can be found are:

- granular activated carbon (GAC) to be used in adsorption columns, and
- powdered activated carbon (PAC) for use in batch adsorption followed by filtration.

GAC can be prepared from hard material such as coconut shell. GAC is commonly used as column filler for gas or liquid treatments and can be regenerated after use. However, one of the problems encountered in the application of adsorption processes to water treatment is the slow intraparticular diffusion in GAC.

In contrast, PAC is obtained when small particles compose the raw material such as wood sawdust and normally mixed with the liquid to be treated and afterwards disposed off. PAC presents a large external surface and a small diffusion distance, therefore it provides faster adsorption velocities and is preferred for adsorption in liquid phase.

2.3. Oil palm shell-derived activated carbon

Wood, bituminous coal, lignite, peat, petroleum residues and coconut shell are some of the conventional starting materials used to produce activated carbons. The selection of the precursor essentially determines the range of adsorptive and physical properties that can be attained in the activated carbon. The choice of precursor is largely dependent on its availability, cost, consistency of quality and purity [23]. In fact, any cheap material with high carbon content and low inorganics can be used as a raw material for the production of activated carbon. Due to the high cost of commercial activated carbons that limits their wide use, currently focus has been given on production of activated carbons from cheap and renewable materials such as agricultural wastes. Agricultural by-products have been proved to be promising raw materials for the production of activated carbons because of their availability at low price and they can be used to produce activated carbons with a high adsorption capacity and considerable mechanical strength [24]. Agricultural biomass is considered to be very important feedstock in virtue of especially two facts: they are renewable sources and low cost materials. Besides, this biomass contains high concentration of volatiles and low ash content which is ideal for creating highly porous structures within the activated carbon matrix [25]. In Malaysia, agricultural by-products are the most abundant biomass resources, exceeding 70 million tonnes annually. The high production rate of biomass throughout the year is mainly due to the high sunlight intensity/time and high rainfall. Palm oil industry is the main contributor of agricultural biomass in Malaysia, generating 94% of the total agricultural biomass [26].

One significant problem faced by the agricultural industries currently is the managing of the by-products and wastes produced. The disposal of the by-products in large quantity is difficult and expensive to the industries. At present, some agricultural by-products are being used as boiler fuel, however large portion of the wastes are either burnt using open burning or dumped aside which will cause environmental pollution as well as harboring pests and diseases. This will result not only in wastage, but also severe economic set back to the industries and the country. Therefore in order to make better use of these abundant agricultural by-products, they need to be utilized effectively to the point that they can be considered as valuable products that will serve as raw materials to support another industry. For this purpose, it is proposed to convert the negative value agricultural by-products into valuable products such as activated carbons. The use of agricultural wastes for the production of activated carbons is very attractive from the point of view of their contribution to decrease the cost of waste disposal, hence helping in environmental protection.

Malaysia is one of the largest palm oil producing countries in the world. One of the significant problems in the palm fruit processing is managing of the wastes generated during the processes. Every year, the oil palm industry generates about 10 million tonnes of solid wastes and this is expected to continue to increase. Palm oil mills in Malaysia produce about 4.3 million tonnes of shell annually [27]. Oil palm shell has been successfully converted into activated carbon and characterized by previous researchers, mainly for removal of gaseous pollutants [28–32]. Recently, oil palm shell-based activated carbon has been commercialized and widely used, e.g. for the adsorption of methane [11], hexavalent chromium [12], copper ions [13], 4-chloroguaiacol [14], phenol [15] and treatment of landfill leachate [16], due to the high adsorption performance. However, the application of this activated carbon in adsorption air-conditioning systems is still limited and hence its potential to be used as the adsorbent in automobile adsorption air-conditioning systems worth to be investigated.

2.4. Preparation and characterization of activated carbon

Basically, there are two main steps in the preparation and manufacture of activated carbon: the carbonization of the carbonaceous raw material in the absence of oxygen to break down the cross-linkage between carbon atoms, followed by the activation of the carbonized product, known as char, for further pore development [24]. Carbonization is a process by which solid residues with increasing content of the element carbon are formed from organic material, usually by pyrolysis in an inert atmosphere. The pores formed during carbonization stage are normally narrowed,

constricted or even blocked by deposited tarry substances. The deposition process occurs while the volatiles are diffusing out of the pore structure into the gas mainstream. Some of the substances may collide with the pore walls, which may lead to hydrocracking that result in carbon deposition [33]. The study of utilizing guava seed-based activated carbon to adsorb methylene blue revealed that carbonization alone yielded a poor adsorbing activated carbon due to the incomplete decomposition of organic constituents as the pores were blocked by carbonization by-products [34].

Activated carbons are commonly characterized by the mode of activation. Knowledge of different variables during activation process is very important in developing the porosity of carbon sought for a given application. Activation is needed to enhance the porosity and to clean out the pores as during carbonization, the pore structures are filled with tar products which decompose and block the pores [35]. Activation process can be divided into three stages based on the variation activity of different parts of the carbon structure. At the initial stage, tarry materials that cause pore clogging are removed thus exposing the surface of the elementary carbon crystal to the activating agent. The second stage involves the burning of elementary crystal followed with disordered and parallel group crystals. This reaction will be terminated when the single crystals are burnt out or when adjoining crystal of the proper orientation is exhausted. The third stage involves deep oxidation which leads to a reduction in the total micropore volume due to the burning of the walls between the neighbouring pores. The process results in the formation of wider pores as a consequence of collapsing walls.

The adsorption performance of an activated carbon is dependent on its properties and characteristics. Therefore, both physical and chemical characterizations need to be carried out on the prepared activated carbons following the standard methods in order to assure its accuracy and consistency. Physical characterization provides technical aspects in terms of surface area, pore volume, pore size distribution and surface morphology. Activated carbon has a unique surface property due to its non-polar or slightly polar nature as a result of the surface oxide groups and inorganic impurities. This has given activated carbon several advantages, such as that it is used to perform separation and purification processes without requiring prior stringent moisture removal. Besides, it adsorbs more non-polar and weakly polar organic molecules compared to other sorbents, due to its large and accessible internal surface. Furthermore, the heat of adsorption on activated carbon is generally lower because only non-specific Van der Waals forces are available as the main forces for adsorption. Consequently, the stripping of adsorbed molecules is easier, resulting in lower energy requirement for the regeneration of the activated carbon [36]. Proximate analysis and surface chemistry are some of the important chemical properties of an activated carbon.

2.4.1. Surface area and pore characteristics

In order to determine the surface area and pore characteristics of activated carbons, nitrogen adsorption–desorption isotherms are monitored at 77 K in the relative pressure range of 10^{-6} to 1 Torr on an automatic adsorption instrument [37]. The most commonly used characterization method to measure the surface area of a material is the BET method suggested by Brunauer, Emmett and Teller [38]. This method is based on adsorption of gas such as nitrogen at low temperatures and conditions which allow adsorption through purely physical forces. The amount of gas required to form a monolayer is obtained from the slope and intercept of the adsorption isotherm. By knowing the probable area occupied by each molecule, the probable area of an adsorbent can then be calculated [39].

Pore volume and the distribution of micropores, mesopores and macropores determine the adsorptive properties of activated carbons. Small pore size will not trap large adsorbates whereas large pores may not be able to retain small adsorbates. Precursors with

a greater content of lignin will develop activated carbons with macroporous structure whereas materials with a higher content of cellulose will produce activated carbons with a predominantly microporous structure [40]. Pore widening was found to take place as a result of wall burning between micropores, which led to an increase in internal porosity and reduction in micropores associated with high surface area. It is well recognized that micropores are characterized by high surface area due to their tremendous number and depth in the activated particles, whereas they constitute a lower fraction of internal porosity which is the pore volume in comparison to mesopores [41].

2.4.2. Particle size distribution

Particle size is one of the important properties of an activated carbon as it can influence the adsorption rate of a particular adsorbate on the activated carbon where the adsorption rate varies reciprocally with the square of the particle diameter [42]. The particle size of activated carbon was found to depend on the type of precursor used as well as the application of the activated carbon.

2.4.3. Surface morphology

Scanning electron microscopy (SEM) is widely used to study the surface morphology, including the pore structure, surface structure and pore arrangement on a material surface. In activated carbon production, SEM analysis can be used to verify the presence of porosity and pore development during pyrolysis and activation processes. From the SEM results obtained [43], the surface of raw pistachio-nut shell was dense without any pores except for some occasional cracks, however after pyrolysis at 500 °C for 2 h, many thin sheets or layers were seen within the char structure, between which were some rudimentary pores due to the release of volatiles. After CO_2 activation at 800 °C for 2.5 h, clear and well-developed pore structure was obtained. In preparing activated carbons from jackfruit peel waste by H_3PO_4 chemical activation, Prahas et al. [44] found from the SEM micrographs that the carbon produced from jackfruit peel waste at 350 °C were non-porous carbons, while the activated carbons produced at 450 °C had cavities on their external surface, which were resulted from the evaporation of the activating agent during carbonization, leaving the space previously occupied by the activating agent.

2.4.4. Proximate analysis

Proximate analysis provides the information on the content of moisture, volatile matter, fixed carbon and ash of a material. Ash content in an activated carbon is considered as impurity, as it may interfere with the carbon adsorption through competitive adsorption and catalysis of adverse reactions [45]. Oil palm shell-based activated carbon was reported to have 1.0–22.6% of volatile matter, 71.5–89.5% of fixed carbon and 5.9–9.5% of ash content [28].

2.4.5. Surface chemistry

Besides pore structure, adsorption characteristics of activated carbons are also determined by the surface chemistry (kind and quality of surface-bound heteroatomic functional groups). The Fourier transform infrared (FTIR) spectroscopy in its various forms is an important and forceful technique which can give useful information about structures. It can provide basic spectra of activated carbons, especially for determination of types and intensities of their surface functional groups. The existence of functional groups such as carboxyls, phenols, lactones, aldehydes, ketones, quinones, hydroquinones and anhydrides on activated carbon surfaces has been postulated. These functional groups determine the acid-base character of activated carbons. The acidic and basic properties are caused by the oxygen-containing groups [36]. Chemical structure of an activated carbon was found to be influenced by the

activation scheme followed. El-Hendawy [20] observed significant changes in the chemical structure of date pit under carbonization where aromatic structures were developed and accompanied by losing most of aliphatic C–H species in the intermediate char product whereas the activated carbons possessed aromatic C=C bonds and oxygen groups. Increasing the activation temperature led to destruction of C=O and C–O species by promoted polyaromatic structures. The main functional groups present in char surface are carbonyl groups (e.g. ketone and quinine) and aromatic rings whereas for carbon activated at high temperature and long activation time, only aromatic rings are remained [18]. The electrical charge of the surface groups may also enhance or decrease the adsorption of the targeted molecules on the carbon surface. If the adsorbate has the same electrostatic charge as that of the carbon surface, repulsion occurs, leading to decrease in adsorption [46].

2.5. Classification of adsorption

Adsorption can be classified into physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption occurs when weak interpartical bonds such as Van der Waals, hydrogen and dipole–dipole exist between the adsorbate and adsorbent whereas chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons [22]. Physical adsorption results from molecular condensation in the capillaries of the solid which usually occurs in gas phase adsorption. There is a rapid formation of an equilibrium interfacial concentration, followed by the rate of diffusion of the solute molecules within the capillary pores of the carbon particles. The rate varies reciprocally with the square of the particle diameter, increases with increasing concentration of solute and temperature, but decreases with increasing molecular weight of the solute [42]. Physical adsorption is a relatively weak adsorptive interaction which is assumed to proceed with zero or negligible activation energy [47].

Chemical adsorption on the other hand results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules [42]. Such interactions are often characterized by a high degree of chemical reaction or molecular configuration, specificity between the adsorbent and the adsorbate that involve specific functional group reactions [47]. It is the result of chemical interaction between the solid and the solute. The strength of the chemical bond may vary considerably and identifiable chemical compounds in the usual sense may not actually form. The adhesive force is generally greater than that found in physisorption and the heat liberated during chemisorption is usually large in sequence of the order of the chemical reaction heat. Chemisorption occurs when strong interparticle bonds are present between adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds [22].

2.6. Adsorption isotherms

Adsorption is the accumulation of a mass transfer process that can generally be defined as material at the interface between solid and liquid phases. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. Isotherm data should accurately fit into different isotherm models to find a suitable model that can be used for the design process. The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Adsorption isotherms are usually developed to evaluate the capacity of activated carbons for the adsorption of a particu-

lar molecule [48]. Adsorption isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of the process for a given application, for selection of the most appropriate adsorbent and for preliminary determination of adsorbent dosage requirements. The isotherm also plays a crucial functional role in predictive modelling procedures for analysis and design of adsorption systems. Several equilibrium models have been developed to describe adsorption isotherm relationships. From the literature, it was found that different adsorbent–adsorbate systems showed different adsorption behaviours where the adsorption data were represented by different isotherm models.

2.7. Adsorption kinetics

In order to design a fast and effective model, investigations are made on adsorption rate. For examination of the controlling mechanisms of adsorption process such as chemical reaction, diffusion control and mass transfer, several kinetic models are used to test the experimental data, adsorption rates are thus sufficient for practical operation [49]. The kinetics of adsorption describes the rate at which the adsorbate is adsorbed on the activated carbon. The adsorption kinetics is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameter is also helpful for the prediction of adsorption rate, giving important information for designing and modelling the process. The prediction of batch sorption kinetics is necessary for the design of industrial sorption columns. The nature of the sorption process will depend on physical and chemical characteristics of the adsorbent system and also on the system conditions [50]. From the literature, it was found that most of the kinetic data fitted well to either the pseudo-first-order or pseudo-second-order kinetic models whereas some other adsorbent–adsorbate systems were reported to follow intraparticle diffusion model and Elovich equation.

2.8. Adsorption thermodynamics

The concept of thermodynamic assumes that in an isolated system where energy cannot be gained or lost, the entropy change is the driving force. The thermodynamic parameters that must be considered to determine the adsorption processes were changes in standard enthalpy, standard entropy and standard free energy due to transfer of unit mole of solute from solution onto the solid–liquid interface, as well activation energy of adsorption. Adsorption reactions are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature. The change in the heat content of a system in which adsorption occurs, the total amount of heat evolved in the adsorption of a defined quantity of adsorbate on an adsorbent, is termed the heat of adsorption ΔH°. While the temperature dependence of equilibrium capacity for adsorption if defined by the parameter ΔH°, the dependence of the rate of adsorption is expressed in terms of the activation energy E. Rate of adsorption is related to the activation energy for adsorption by the Arrhenius equation [7].

3. Adsorption versus vapour compression systems in automobile

Typically, adsorption system has some features in common with the conventional vapour-compression system (Fig. 1) but differ in a few aspects. The main different between both systems is that the mechanical compressor in vapour-compression system is replaced by a thermally driven adsorption compressor. Hence, the ability to be driven by heat during the desorption process makes adsorption system an attractive solution for electric energy savers. Another different between these two systems is that heat source
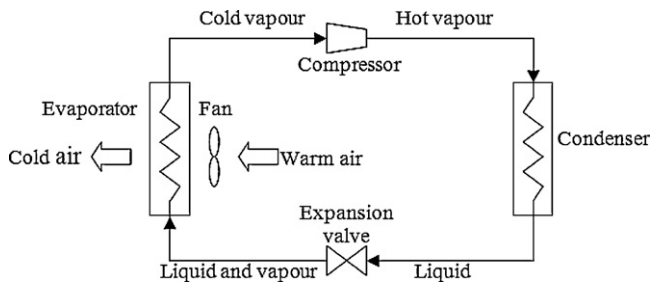
Fig. 1. Schematic diagram of conventional vapour-compression system in automobile.

must be introduced in adsorption system to retrieve the refrigerant vapour from the adsorbent before the refrigerant enters the condenser. While conventional automobile air-conditioner normally uses shaft work of the engine to drive a mechanical compressor, which increase the engine load and thus rise the engine operating temperature and also fuel consumption.

Adsorption system can be operated without any moving parts other than magnetic valve when fixed adsorbents bed is employed. This means that adsorption system is mechanically simple, low vibration, high reliability, and long lifetime. Two or more adsorbers are needed and operated intermittently in adsorption system to produce a continuously flow of refrigerant into the evaporator, while only one mechanical compressor is use in vapour-compression cycle. During the operation of the continuous adsorption cooling system, one of the adsorber is in heating phase (regeneration) while the other(s) is/are in cooling phase (adsorption) and vice versa. The primary drawback of conventional vapour-compression system is that it still uses HCFC refrigerants, which can contribute to depletion of the Earth's ozone layer. In countries adhering to the Montreal Protocol, HCFCs are due to be phased out and going to replace by ozone-friendly HFCs. However, systems using HFC refrigerants tend to be slightly less efficient than systems using HCFCs. Also it is to be noted that although HFCs are ozone-friendly, it still poses large GWP because they remain in the atmosphere for many years and capable to trap heat more effectively than carbon dioxide. Table 1 shows the differences between the conventional vapour-compression system and the adsorption system.

4. Theoretical consideration of adsorption air-conditioning

Generally, air-conditioning system can be classified as electrical system and thermal system, as illustrated in Fig. 2. Electrical system consists of vapour-compression system and peltier element, whereas thermal system consists of heat transformation and thermo-mechanical process. Heat transformation, which also known as sorption system, includes closed and open cycles. Closed cycles are referred to absorption and adsorption cycles, while open cycles are referred to desiccant cycle. This review paper will focus only on the adsorption cycle mainly for automobile air-conditioning purpose due to the fact this cycle required low regeneration heat compared to absorption cycle. In general, adsorption cycle can be categorized into two main cycles; namely

intermittent cycle and continuous cycle. Intermittent cycle seems not suitable to be employed in automobile application due to the fact that it cannot provide continuous cooling as needed. Thus, a continuous cycle could be adopted here to generate continuous cooling effect by using two or more adsorbers that operate intermittently.

4.1. Adsorption cycle

4.1.1. Basic of adsorption

Generally, adsorption is a process where molecules of a gas or liquid contact and adhere to a solid surface. This process is always exothermic, where heat is liberated. The substrate on which adsorption take place is called as adsorbent, whereas the material concentrated on the surface of the adsorbent is called as adsorbate. Adsorbents are the matters that contain a lot of miniscule internal pores as small as nanometres. Adsorption mechanisms can be categorized into two types; namely physical adsorption and chemical adsorption. Physical adsorption is the type of adsorption in which the forces involved are intermolecular forces or Van der Waals forces. Chemical adsorption, on the other hand, is the type of adsorption in which the forces involved are covalence or ionic forces between the adsorbing molecules and the adsorbent. As covalence or ionic bonding is normally greater than Van der Waals bonding, more heat is liberated when chemical adsorption occurred. Besides, the process of physical adsorption is reversible, while chemical adsorption process is irreversible. Typically, an adsorption cycle applied in air-conditioning or refrigeration does not use any mechanical energy, but only heat energy from waste heat, solar or any means of heat. Adsorption unit usually consists of one or several adsorbers, a condenser, an evaporator and associated to the heat source. This cycle is basically an intermittent because cold production proceeds only during part of the cycle if only one adsorber is utilized. Nevertheless, when more than one adsorber is used, this cycle can be operated out of phase and generate a quasi-continuous cooling effect. For situation where all the energy required for heating the adsorber is provided by the heat source, the cycle is called as single effect cycle. Likewise, double effect cycle can be processed by using two or more adsorbers. In double effect cycles some heat is internally recovered between the adsorbers, which enhance the cycle performance. Various types of adsorption cycles have been studied extensively by Wang [51]. Some of the common adsorption cycles are basic cycle, mass recovery cycle, continuous heat recovery cycle, thermal wave cycle, cascade multi effect cycle, and hybrid heating and cooling cycle.

4.1.2. Ideal adsorption cycle

Basically, an ideal adsorption cycle can be well represented by using Clapeyron diagram [52], as shown in Fig. 3. At point 1, the ideal adsorption cycle start under low pressure P_5 and low temperature T_1. The adsorbent and adsorbate is then heated from point 1 to point 2 at higher pressure P_3. Continue heating of the adsorbent and adsorbate from point 2 to point 4 will cause some adsorbate vapour to be desorbed from the adsorber and then condensed through a condenser at point 3. After that, the adsorbate in liquid form is flowed into the evaporator from point 3 to point 5 at

Table 1
Comparison between vapour-compression system and the adsorption system.

Vapour-compression system	Adsorption system
• Mechanical compressor is used to compress the refrigerant vapour between the evaporator and the condenser.	• Thermal compressor is used to compress the adsorbate by adsorbing and desorbing adsorbate vapour.
• Mechanical compressor is driven by the shaft powered by the engine.	• Waste heat from the automobile engine can be utilized to operate the system.
• CFC and HCFC are usually used as refrigerant.	• Water, methanol or other alternative clean refrigerant can be used.
• Compressor failure can be due to wear.	• Less moving parts.
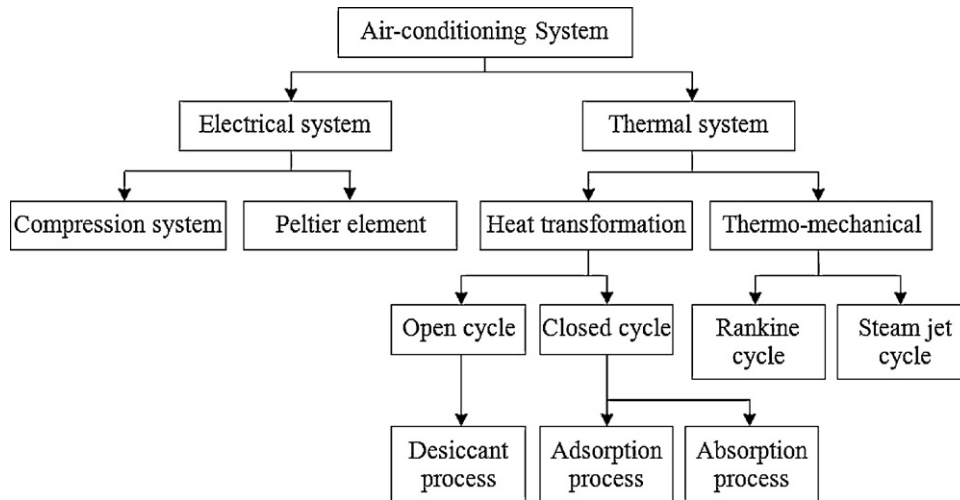
Fig. 2. Air-conditioning technologies.

Fig. 3. Ideal adsorption cycle [52].

4.1.3. Thermodynamic analysis of adsorption cycle

In general, the operation of adsorption cycle involves the processes of isosteric heating, desorption, isosteric cooling and adsorption. A simple adsorption cycle indicating all the heat transfer for a complete cycle and its T-S diagram [53] are as illustrated in Fig. 4(a) and (b), respectively. Heat (Q_d) is supplied to release adsorbates from the adsorbent at high temperature T_d during the desorption process. The desorbed adsorbate vapours are then travel to the condenser, where it is condensed by releasing heat (Q_c) to the surrounding at temperature T_c. When the liquid adsorbates reach the evaporator, it evaporated and heat (Q_e) is adsorbed from the surrounding to produce cooling effect at lowest temperature T_e. During the adsorption process, these vapours are adsorbed back by the adsorbent by released heat (Q_a) at temperature T_a. This cycle can be repeated by just heating and cooling of the adsorbent beds intermittently.

4.2. Adsorbent–adsorbate pairs

In general, selection of an appropriate working medium is a crucial factor for the successful operation of an automobile adsorption air-conditioning system as the performance of this system varies over a wide range by using different working pairs at different temperatures. In order to choose the best adsorbent, the following factors need to be considered:

- good thermal conductivity and low specific heat capacity to decrease the cycle time,
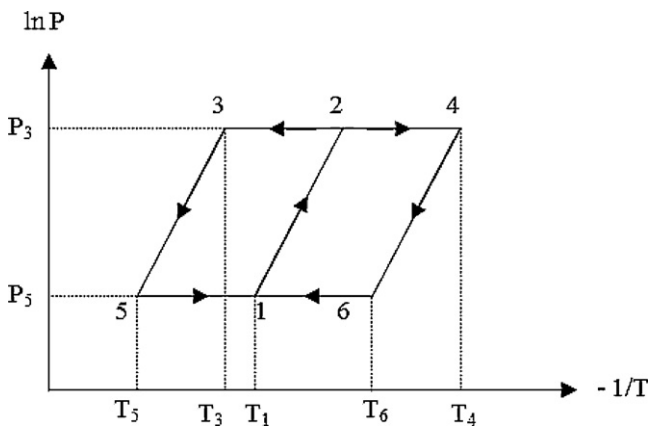
lowest pressure P_5 and temperature T_5. When the adsorbate liquid enters the evaporator, it vaporized spontaneously due to lower pressure in the evaporator. The evaporator, which serves as the heat absorption component, is uses to remove heat from the cooling space and also dehumidification. Meanwhile, the desorption process end when the adsorbent heated to the highest temperature T_4. Decreasing in temperature to T_6 cause the pressure dropped to P_5. The evaporator is then connected to the collector, where adsorption of the adsorbate vapour occurs. At the same time, the adsorbent is cooled from point 6 to point 1 and the cycle repeats again.
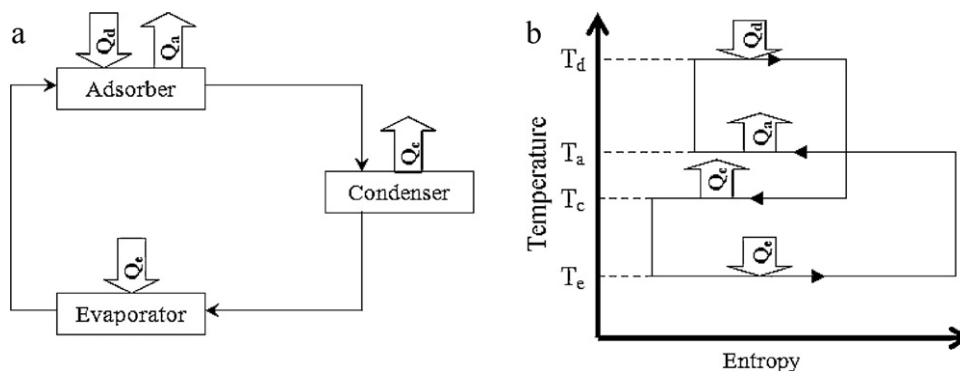

Fig. 4. (a) A simple adsorption cycle; (b) T-S diagram [53].

Table 2
Some adsorbent–adsorbate pair and their heat of adsorption [54].

Adsorbent	Adsorbate	Heat of adsorption (kJ/kg)
Silica gel	Water	2800
	Methyl alcohol	1000–1500
Zeolite (various grades)	Water	3300–4200
	Carbon dioxide	800–1000
	Methanol	2300–2600
	Ammonia	4000–6000
Activated alumina	Water	3000
Activated carbon	Ethene	1000–2000
	Ethanol	1200–1400
	Methanol	1800–2000
	Water	2300–2600
	Ammonia	2000–2700
Calcium chloride	Methanol	–

- high adsorption and desorption capacity to achieve higher cooling effect,
- no chemical reaction with the adsorbate used, and
- widely available and also low cost.

While the preferable adsorbate should have the following desirable thermodynamics and heat transfer properties:

- high latent heat per unit volume to increase the cooling effect,
- high thermal conductivity to decrease the cycle time,
- chemically stable within the working temperature range, and
- non-toxic and non-corrosive.

Suitable adsorbate must be choosing carefully in order to achieve high performance of the adsorption system. The most common adsorbate–adsorbent pairs utilized are activated carbon–methanol, activated carbon–ammonia, zeolite–water, zeolite–organic refrigerants, silica gel–water, salts–ammonia, metal–hydrogen, etc. Some of the common working pairs together with their heat of adsorption [54] are as listed in Table 2.

4.3. Performance analysis

The performance of the adsorption system is usually assessed by using two performance factors; namely coefficient of performance (COP) and specific cooling power (SCP). COP is defines as the amount of cooling produced by the adsorption cooling system per unit heat supplied [55,56] as given below:

$$COP = \frac{Q_e}{Q_d} \qquad (1)$$

where Q_e is the quantity of heat transferred through the evaporator, and Q_d is the quantity of heat adsorbed by the adsorber during desorption phase.

While SCP is defined as the ratio between the cooling production and the cycle time per unit of adsorbent weight, as given follow:

$$SCP = \frac{Q_e}{t_c m_a} \qquad (2)$$

where t_c is the cycle time, and m_a is mass of the adsorbent.

Since SCP is correlates to both the mass of adsorbent and the cooling power, it determines the size of the system. For a small cooling load, higher SCP values indicate the compactness of the system.
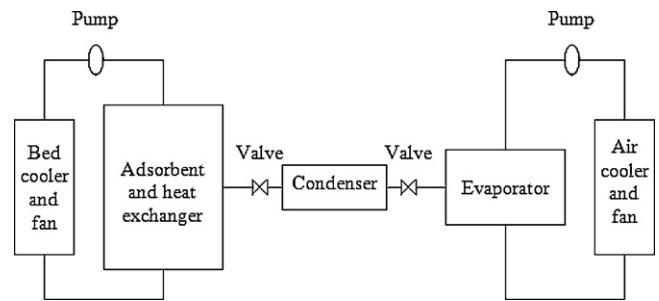
Fig. 5. Schematic diagram of adsorption air-conditioning system for electric vehicle [59].

5. Application of adsorption technologies in automobile air-conditioning

Duran [57] has disclosed an apparatus employed chemisorptions principle as a vehicle air-conditioner. Chemisorptions are the type of adsorption in which the forces involved are covalence or ionic forces between the adsorbing molecules and the adsorbent. The drawback of such system is that very high temperature is needed during regeneration process to release the adsorbate. A preliminary study has been carried out by Suzuki [58] to elucidate the technological limits associated with the application of adsorption cooling systems to automobiles. The working pair used in the study was zeolite-water and exhaust heat as the thermal energy input to the system. Suzuki study showed that a cooling capacity of 2800 W/kg per one unit of adsorbent bed is expected if the UA of 100 kW/(mK) could be achieved and adsorption–desorption cycles of 60–60 s could be adopted. However, the author just did some simulations study and no experimental work being carried out to verify his claimed.

Aceves [59] has carried out an experimental analysis of the applicability of an adsorption system for electric vehicle air conditioning, as shown in Fig. 5. The COP of the system, with zeolite and water as a working pair, was approximately 0.28. His studies indicated that conventional compression air conditioners were superior to adsorption systems due to their higher COP and are more compact. The drawback of using zeolite–water as a working pair is that a very low operating pressure is needed. Meanwhile, Bhatti et al. [60] have disclosed the use of zeolite to dehumidify the air by using desiccant wheel. This wheel consists of two sections; the first section dehumidified the air before supply to the evaporator of the conventional compression air-conditioning system while regeneration of the saturated zeolite by using heated air is take place in another section simultaneously. Unfortunately, these systems are not currently used because the wheel is too large to be installed in a typical automobile.

Sato et al. [61] have presented a multiple-stage adsorption air-conditioning system for vehicle. They also reveal that two or more adsorbers are utilized during adsorption and regeneration processes, respectively. Although the efficiency of the multiple-stage adsorption system improved, the size of the system also increased and thus adds complexity to its control system. Denniston [62] has disclosed dehumidification systems to dehumidification and humidification of air prior to its entry into the vehicle interior. In addition, he also disclosed various bed configurations to dehumidify the air and regeneration the bed by utilizing heat from the engine. The application of electric heating element to regenerate the adsorbent was disclosed by Kirol and Rockenfeller [63] and Tanaka et al. [64]. Although their system may be effective during regeneration process, the utilization of electric heating element adds complexity to the adsorption system. This is because the heating element must be properly mounted to the adsorbent bed in
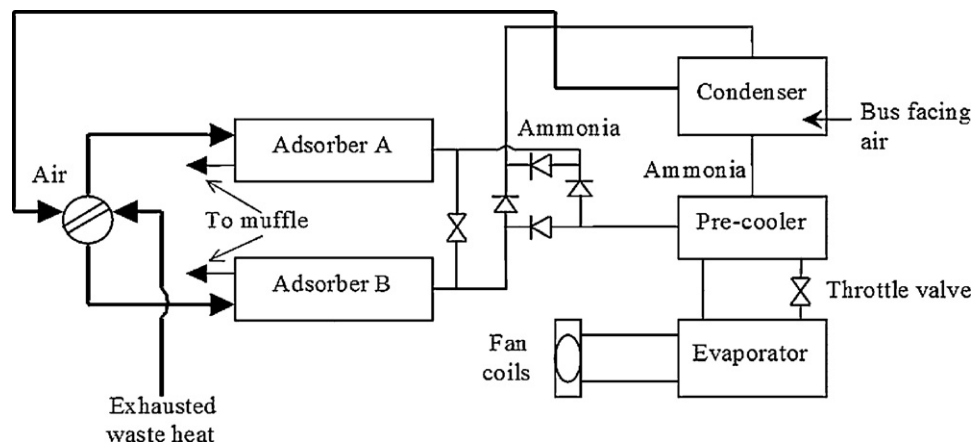
Fig. 6. Schematic diagram of adsorption air conditioner for buses driven by the waste heat from exhausted gases [51].

order to create a better heat transfer between the adsorbent and the heating element. Besides, a proper wiring is needed.

Li and Ling [65] have presented a numerical study of the dynamic performance of an adsorption cooling for automobile waste heat recovery. It was found that the SCP is more sensitive to parameter changes than the COP and by improving the overall heat transfer coefficient is the most effective way to increase SCP. Structural characteristics of the adsorption air conditioning system driven by exhausted gas in automobiles have been presented by Tan and Wang [66]. They found that the heat pipe effect is apparent in isosteric heating and isosteric cooling stages, which can greatly enhance the heat transfer effectiveness. They also discussed several factors that influence the performance of the system, such as working conditions and physical characteristics of adsorbent. Besides, they concluded that by enhancing the effective thermal conductivity of the absorber and decreasing the contact resistance are the key technologies in this system. Meanwhile, Zhang [56] has described an experimental intermittent adsorption cooling system driven by the waste heat of a diesel engine. Zeolite 13X–water is used as the working pair and a finned double-tube heat exchanger is used as the adsorber. The COP and SCP of the system are 0.38 and 25.7 W/kg, respectively.

Wang [51] has reported an adsorption air conditioning for a bus driven by using waste heat from exhausted gases. The working pair for this system is activated carbon-ammonia with the cooling power of 2.58 kW and COP of 0.16. The design configuration of the overall system was shown in Fig. 6, which consisted of two adsorbers (Adsorber A and Adsorber B). The activated carbon is pressurized to the density of about 900 kg/m in order to fill more adsorbent into the adsorber. The total weight of the two adsorbers is about 248 kg and occupied about 1.0 m^2. The disadvantages of this system are it is bulky and heavy. Nagatomo et al. [67] have described a vehicular adsorption type air-conditioner capable of enhancing the heat radiation performance of an outdoor unit and enhancing the cooling capacity. The outdoor unit is installed on a vehicle roof top. Much more fresh air not affected by exhaust heat from an engine or the ground heat is allowed to flow in the outdoor unit. Thus, the temperature of liquid refrigerant passing through the outdoor unit can be dropped and the cooling capacity of the vehicular adsorption type air-conditioner can be enhanced. As a continuation part, Nagatomo et al. [68] have disclosed a method for saving the water feeding power based on the temperature of cooling liquid and heat transfer fluid in the vehicular adsorption type air-conditioner. The air-conditioner comprises a fourth pump to allow cooling water heated by an engine to flow into a desorption step of an adsorber. First and second pumps drive second heat transfer fluid cooled by an outdoor unit to flow into an adsorp-

tion step of the adsorber. A third pump drive third heating transfer fluid cooled by the evaporator to flow into an indoor unit. Water temperature sensors detect temperature of the second heat transfer medium and the third heat transfer fluid. The first to fourth pumps are controlled to adjust the water feeding power based on temperature information detected by the water temperature sensors. However, the utilization of pumps in vehicular adsorption type air-conditioner adds the complexity of the system and also caused system malfunction due to pump failure.

Experimental studies on the practical performance of an adsorption air conditioning system powered by exhausted heat from a diesel locomotive have been presented by Lu et al. [69]. The system (Fig. 7) was incorporated with one adsorbent bed and utilizes zeolite-water as a working pair to provide chilled water for conditioning the air in the driver's cab of the locomotive. Their experimental results showed that the adsorption system is technically feasible and can be applied for space air conditioning. Under typical running conditions, the average refrigeration power ranging from 3.0 to 4.2 kW has been obtained. However, this system may not suitable to be mounted on automobile due to its size and also high temperature is required during regeneration process. Meanwhile, Inoue et al. [70] have described a system, which used cooling water from internal combustion engine that includes a compressive refrigerator and an adsorption type refrigerator. The compressive refrigerator is used to control the temperature of the air to be blown into a passenger compartment of the vehicle. The adsorbent generates adsorption heat when the adsorbent adsorbs the adsorbate, and desorbs the adsorbate when the adsorbent is heated by coolant
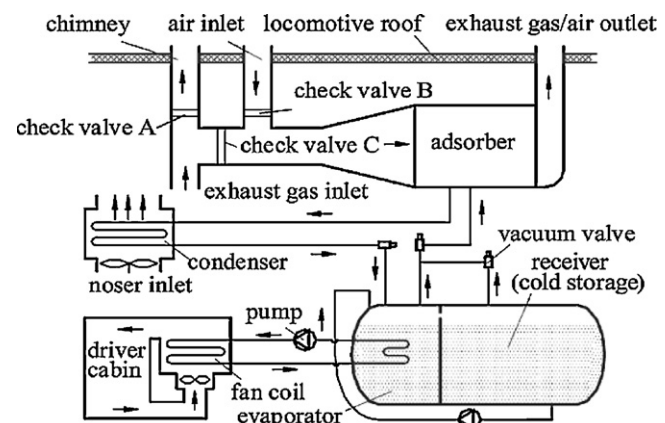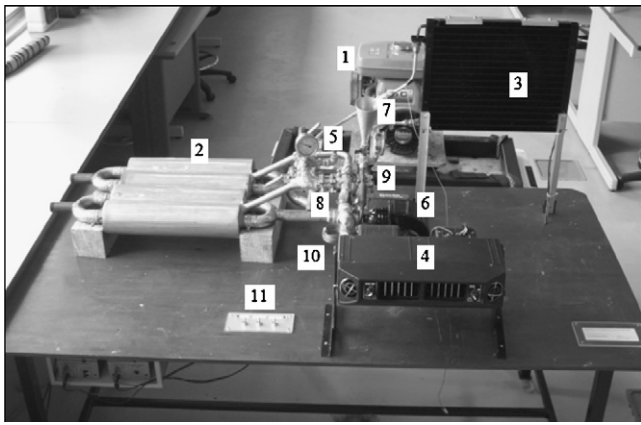

Fig. 7. Schematic diagram of locomotive driver cabin air-conditioner [69].

Fig. 8. Laboratory prototype; (1) four-stroke petrol engine, (2) two thermal compressors packed with activated carbon, (3) air-finned-tube heat exchangers (condenser), (4) air-finned-tube hanging type evaporator, (5) compound vacuum gauges, (6) 12 V DC blower, (7) funnel (adsorbate inlet), (8) check valves (control adsorbate flow), (9) three-way valve (control exhaust gas/cooling air flow), (10) pressure regulating device (orifice tube) and (11) switch (DC power supply).

water from the internal combustion engine. The air to be blown into the passenger compartment is heated by the adsorption heat of the adsorbent, and then the air is cooled by evaporation latent heat of the adsorbate. On the other hand, Henning and Mittelbach [71] have disclosed an adsorption heat pump for air-conditioning a passenger car. Their system is based on a quasi-continuous operation of adsorption heat pump with the used of cold and heat accumulators.

Lambert and Jones [72] have traced the conceptual and embodiment design of an exhaust-powered adsorption air conditioner. In addition, adsorption cooling is then compared with other thermally powered cooling technologies (stirling, absorption and thermoelectric), demonstrating that adsorption is the best alternative in terms of size and mass. They have presented that COP of the adsorption system can be boosted from 0.30–0.40 with single effect heating to 0.50–0.65 with double effect heating. Meanwhile, Seiji et al. [73] have carried out a study on adsorption refrigerators for automobiles by using temperature dependency of adsorbents. In this study, appropriate characteristics of adsorbent were estimated. It was found that at high ambient temperature conditions, the relative humidity in adsorption stage will be smaller than that in desorption stage. As a result, the adsorption isotherm should have temperature dependency and will be estimated from the Clausius–Clapeyron's equation. A prototype of compact sorption generator using an activated-carbon–ammonia pair based on a plate heat exchanger concept has been designed and built by Critoph et al. [74] in Warwick University. They have reported that a pair of the generators loaded with ∼1 kg of carbon in each of two beds can produce an average cooling power of 1.6 kW with 2 kW peaks.

Recently, a laboratory prototype of exhaust heat-driven adsorption air-conditioning system for automobile (Fig. 8) has been built successfully, commissioned and laboratory tested [53,75]. The system [53] consisted of two adsorbers, a blower, an evaporator with

a blower, a condenser with a fan, orifice tube, valves and an engine. This prototype can produced cooling effect continuously, where two identical adsorbers were installed and operated intermittently. An engine was used to supply exhaust gas to heat one of the adsorber during desorption phase. At the same time, a blower was used to blow air through the other adsorber to initiate adsorption phase. The cycle time of the system is set to approximately 20 min, where the desorption and adsorption phases is around 10 min. The average chilled air temperature that can be achieved was around 22.6 °C when the average cooling coil temperature was around 11.4 °C. The COP and SCP of the prototype were calculated to be approximately 0.2 and ∼400 W/kg of adsorbent, respectively. Table 3 summarizes some of the developments in adsorption air-conditioning technologies in automobile.

6. Outlook of automobile adsorption air-conditioning

Generally, adsorption refrigeration technologies have been widely studied in academic field as well as in industry sectors. As reported in the cited journals and patents, these technologies have also been studied for automobile air-conditioning applications. However, it has not commonly used in today's automobiles due to yet a few limitations. One of the main limitations is due to the fact that most currently available adsorbents have low adsorptive–desorptive capacity, which could lead to huge system requirement and thus quite difficult to be installed into automobiles. In order to overcome this limitation, new synthetic or natural adsorbents with higher adsorptive capacity should be invented to build a compact system. Besides that, heat transfer rate inside the adsorber normally is quite slow and thus increase the overall cycle time. Coated adsorbent technology and heat pipe could be an alternative to improve the system efficiency by reducing the cycle time and overall heat transfer rate. Another limitation is that commonly used adsorbates have low latent heat and high boiling point, which cause low cooling effect generated. Therefore, new type of adsorbates that have less impact to the environment shall be used. The employment of adsorption air-conditioning technology could be one of the best options to replace conventional compression system that commonly used in present automobiles. The reasons follow:

- the potential used of exhaust heat help to decrease the quantity of carbon dioxide emission from combustion of the fossil fuels as the engine load was decreased, thus reduce the overall operational cost,
- clean refrigerants (instead of using CFCs and HCFCs) that has zero ozone depletion and global warming potentials can be used as a working fluid,
- low regeneration temperature (less than 150 °C) could be used to operate the system, and
- less moving parts, low maintenance cost and simple system structure make it attractive for automobile application.

Apart from compact in sizing, a practical *near future* automobile adsorption system would perhaps able to achieve a COP range from 0.5 to 0.8, with SCP ≥ 1 kW/kg.

Table 3
Some of the developments in automobile adsorption air-conditioning technologies.

Investigators	Heat source	Working pairs	COP	SCP (W/kg)	Remarks
Suzuki [58]	Exhaust heat	Zeolite/water	–	–	Simulation
Aceves [59]	Electric heater	Zeolite/water	0.28	–	Experiment
Tan and Wang [66]	Exhaust heat	Activated carbon/methanol	–	–	Simulation
Zhang [56]	Diesel engine	Zeolite 13X–water	0.38	25.7	Experiment
Wang [51]	Exhaust heat	Activated carbon/ammonia	0.16	20.8	Experiment
Lu et al. [69]	Exhaust heat	Zeolite/water	0.18–0.21	–	Experiment
Leo and Abdullah [53]	Exhaust heat	Activated carbon/methanol	0.19	396.6	Experiment

7. Conclusions

Recent research has shown that new evolvement in adsorption technology has a promising potential to be adopted in automobile air-conditioning purpose. The technology is expected to be practical when further improvements are done to overcome some of the limitations mentioned above. Using clean refrigerants in adsorption air-conditioning systems will reduces the production of unwanted ozone depleting substances, such as CFCs and HCFCs. As such, adsorption air-conditioning system for automobile should be seriously looked into. Besides it being environmentally friendly, low maintenance cost could be expected. By implementing the adsorption air-conditioning system powered by waste heat may provide a comfort for the driver and/or passengers by lowering the air temperature level and also for air ventilation during driving or parking.

Acknowledgements

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